Advanced NMR Techniques in Solution and Solid State
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Module-57
Magic Angle Spinning
Lecture – 57

Welcome back all of you. Since last one or two classes we started discussing about solid state NMR. I briefly introduced you what are the interaction parameters that are present in solid which gets averaged out in solution state. For example dipolar couplings both homonuclear and heteronuclear chemical shift anisotropy, J anisotropy, all these parameters are averaged out in solution state, but they are present in the solid state in full form.

I said full form because it can be also reduced by dropping the molecule in a partially ordered environment, that is what I said in some liquid crystals, but in solids because the order parameter is 1 it is fully present and it complicates the NMR spectrum a lot. And why it complicates the NMR spectrum, that is what we discussed, because all these parameters are orientation dependent.

It depends upon a factor called 3 cos square theta – 1 divided by 2 where theta is the angle that internuclear vector makes with respect to the magnetic field, as far as the dipolar interactions are concerned. If you go to chemical shift anisotropy, I said the charge distribution at the site can be considered like an ellipsoid. It depends upon the orientation of the ellipsoid, direction of the ellipsoid; that is also orientation dependent. It depends on 3 cos square theta – 1 by 2.

As a consequence, I said this also depends upon 3 cos square theta – 1 / 2. And then I also said, I gave an example to see that what happens if I vary the theta. In the case of dipolar couplings, we kept on varying the angle theta from parallel orientation to perpendicular orientation for a given internuclear vector and we found that doublet components alpha and beta, the doublet separation was quite large, kept on reducing, at a particular angle they both of them collapse. And this started increasing again, so this is what we observed and at a particular angle it collapsed and gives rise to a singlet. And all possible, infinite orientations are present in a given molecule in the powder form, varieties of orientation of internuclear vectors are there. As a consequence, several spectra will be present which overlap. As a consequence you are going to get what is called a powder pattern; that is what I said. Same thing in the case of chemical shift anisotropy also. Depending upon the orientation of the ellipsoid, the chemical shift for a particular molecule can keep on varying, the position keeps on changing. And I took the example for three possible orientations for one of the molecules, I showed how the chemical shift changes, because again it has infinite possible orientations. The overlap of them gives rise to a powder pattern.

We saw two types of powder pattern for chemical shift anisotropy. One is axially symmetric other is axially asymmetric. Axially asymmetric pattern we clearly saw we have sigma 11, sigma 22, sigma 33; these are the principal components of the chemical shift anisotropy tensor, which are obtained after transformation into a frame of reference, where we get only three diagonal elements of the CSA; that is what we discussed.

For axially symmetric again we have only two sigma 11 = sigma 22, other one is different. Two of them are equal and third one is different; we discussed all those things and I said, I gave an expression called Dij = 1 over rIJ cube into spin part into space part. I said rIJ is internuclear distance. All these three factors are products; they multiply among themselves then I said rIJ can become infinity, when we consider two spins which are dilute, because probability of finding both of them; for example carbon 13 and carbon state 13 is one in 10,000. As a consequence we can say these spins are separated by infinite distance. So, rIJ become infinity; the dipolar coupling become 0. Or in other words we can say for dilute spins the dipolar couplings probability of seeing is very, very low.

Now we discussed about the space part and the spin part. Using these things, we can also average out, that is what we said. Space part is the rotation of the sample at a given angle of at particular speed or some speed. Then I said the second order interaction tensors, like heteronuclear dipole coupling, CSA everything, will get averaged out. In the spins part we can also do the same thing by making the spins to go through all such similar rotations in the spin space. And we can averaged out some type of dipolar coupling, the homonuclear dipolar coupling; I said that. Today we will go further and try to understand what is magic angle spinning.

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$\frac{3\cos^2\theta-1}{2}$

MAGIC ANGLE SPINNING (MAS)

NPTEL, IISc

The sample is put into the rotor, which is kept tilted at 54.7° with respect to the external magnetic field

The bearing and driving
res
are adjusted to get the
spinning speed

Now I will tell you what is a magic angle spinning. In magic angle spinning, what you will do is take a sample; put it in a rotor like this of length let us say 1 to 1.2 centimeters, with inner diameter which is varying from 7 mm to 4 mm to 2.5 mm, 3.2 mm, varieties of or diameters you can have. Put this sample into the magnetic field. Align this rotor axis of rotation of this rotor with respect to the magnetic field, at an angle called magic angle, which is 54.7 degrees. Why this 54.7 comes, put it into the equation 3 cos square theta – 1 divided by 2. Then you will find out at angle 54.7; this term goes to 0. That is why this angle is called a magic angle.

Align this rotor at that particular angle, and then start spinning with such a speed then you can eliminate some interactions. This is called magic angle spinning; and how do you do that? By using the compressed air the high pressure air; the bearing and driving pressure to adjust the spinning speed to make this sample rotate at certain spinning speed, of the order of several kilohertz.

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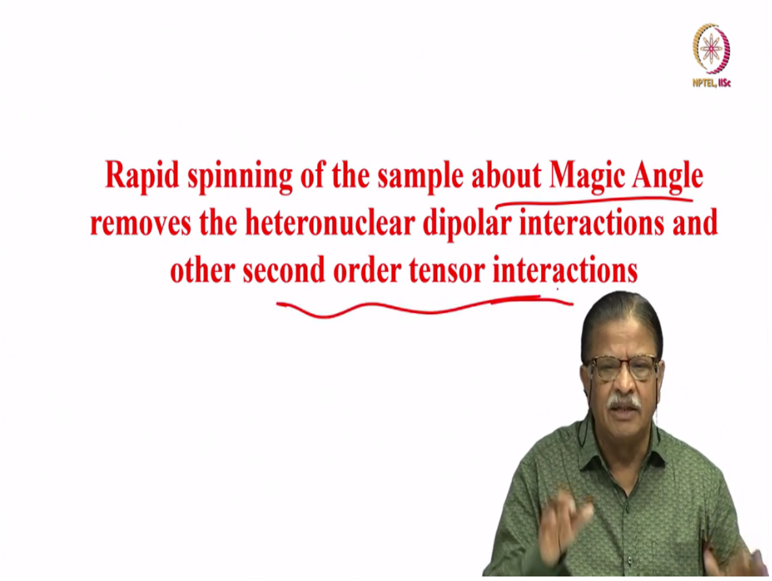

Rapid spinning of the sample about Magic Angle removes the heteronuclear dipolar interactions and other second order tensor interactions

So, rapid spinning of the sample about the magic angle, what it does? it removes heteronuclear dipolar interactions, heteronuclear dipolar couplings. And any other second rank interaction tensor which are present; they also will be removed; and CSA also would be removed.

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Typical Sample Holder for MAS

- 4 mm Rotor
- Flutes on cap for spinning
- Strobe mark for spinning speed indication
- Filling funnel

Quantity : around

Just to show you a typical sample holder for magic angle spinning, this is like this. It is a rotor and if we take NMR for the solution state it will be like this, a 5 millimeter tube of length about nearly 10 to 12 centimeters and inner diameter about 5 millimeter or sometimes 3 millimeter also are there. But in the case of solid state, since we have to rotate this sample at a rapid speed, the sample is taken in a container like this called rotors.

It can vary in diameter, internal diameter from 4 mm to varieties of diameters, which I am going to show you as we go ahead. And there will be a cap with what are called flutes, like this. And then using the flutes what we do is we will rotate the sample at a high speed; and we will put a marker here at this side, so that we can measure the spinning speed. So, all these things are little details; but do not worry. I want you to get the feeling where how you put the sample in a particular material called rotor, how does it look.

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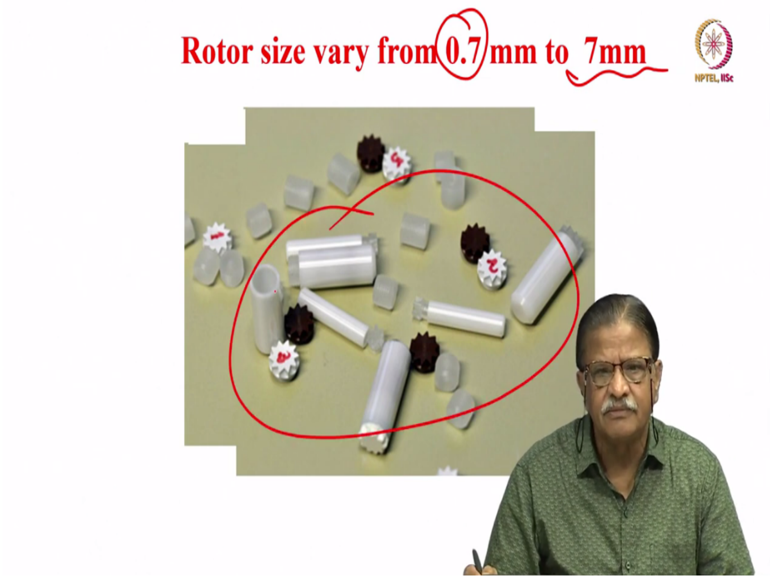

Rotor size vary from 0.7 mm to 7mm

And varieties of rotor sizes are available from 0.7 mmto even 14 mm are also there. These are all the rotors of varieties of sizes.

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Spinning speed varies with the inner diameter of rotor

And then spinning speed depends upon this inner diameter of the rotor. You can look at this, it is 7 millimeter rotor which is taken from Physics Today, October 2016. This can give you spinning speed up to 8 kilohertz. If you go to 4 mm rotors you can go up to 15 kilohertz, go to 3.2 mm rotor you can go up to 23 kilohertz. you can go to 2.5 mm rotor, you can go up to 35 kilohertz. If you go to 1.3 mm you can go to 60 kilohertz and 0.7 mm can go up to 111 kilohertz.

Now with attempts are there to increase the speed even further. So, you understand, look at the size of this rotor. It is very, very small 0.7 millimeter inner diameter, within which you have to put the sample.

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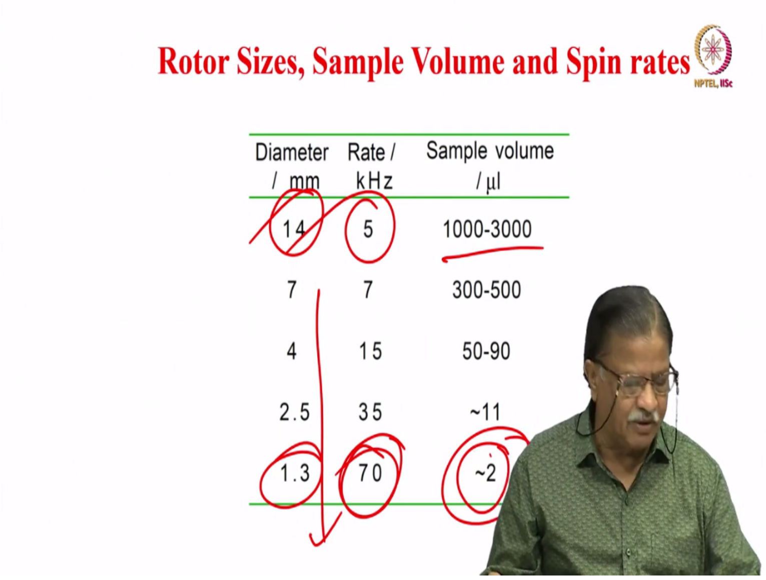

Rotor Sizes, Sample Volume and Spin rates

Diameter / mm	Rate / kHz	Sample volume / µl
14	5	1000-3000
7	7	300-500
4	15	50-90
2.5	35	~11
1.3	70	~2

And how much sample quantity you put it also matters. For example if you take a 1.3 millimeter diameter rotor you can put only 2 micro liter sample, that is enough. You can look at the size and the quantity of the sample that you are utilizing. One advantage is you can go to high spinning speed; that has lot of disadvantages; I will discuss as we go further, but sample quantity is less.

In the signal to noise ratio there is a compromise since quantity of the sample is less. And on the other end go to, let us say 14 millimeter diameter rotor, you can spin maximum of 5 kilohertz; but you can take sample of 1 to 3 ml. It gives very good signal to noise ratio because sensitivity you can enhance a lot because of the sample quantity. So, there is a compromise on all those things.

I want you to understand as the size of the rotor increases, the spinning speed increases, but the sample quantity decreases. So there is a compromise you have to work out, depending upon what you require.

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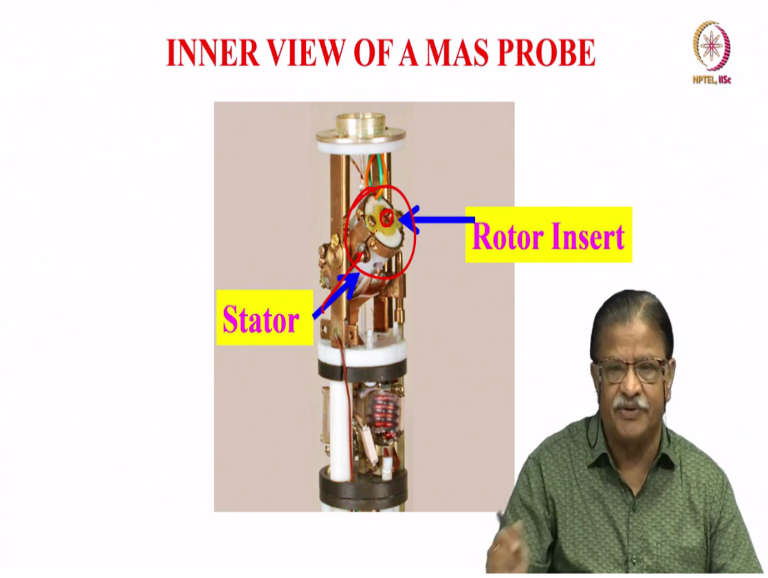

INNER VIEW OF A MAS PROBE

This is a inner view of a magic angle spinning probe. It is different from the conventional liquid state probe. This is where rotor is going to sit, this is called a stator and the rotor goes and sits inside this. There is a small diameter appropriate to the size of the rotor, you have appropriate probe. This is let us say about 2.5 mm rotor, it goes and sits into this, this is the inner view of it.

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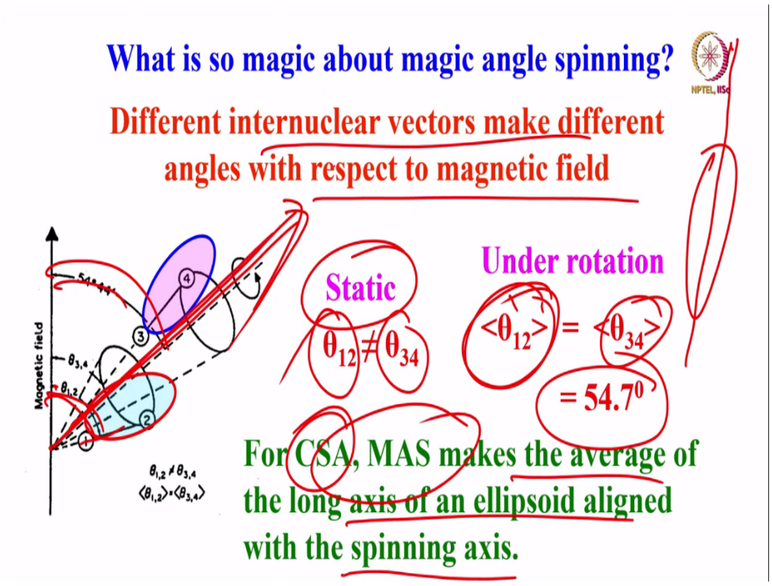

What is so magic about magic angle spinning?

Different internuclear vectors make different angles with respect to magnetic field

Static

$\theta_{12} \neq \theta_{34}$

Under rotation

$\langle\theta_{12}\rangle = \langle\theta_{34}\rangle$

$= 54.7^0$

For CSA, MAS makes the average of the long axis of an ellipsoid aligned with the spinning axis.

And then what is so magic about the magic angle. Okay I have put the sample in a rotor. Rotor is aligned at an angle with respect to magnetic field and starts spinning at some rapid speed. Some speed 20, 30 kilohertz whatever the speed, I can achieve in a particular rotor. Then what is going to happen? look at it. If you look at it different internuclear vectors are there, which can make different angles with respect to magnetic field, before spinning the sample, you understand.

You take a rotor and put the sample in this, innumerable number of internuclear vectors you can see, because in a powder samples varieties of orientations are possible. This was simply put the rotor into this stator. Now I can consider internuclear vector between 3 and 4, let us say, that is internuclear vector 3 and 4 here and this is making certain angle with respect to magnetic field.

And another internuclear vector here 1, 2 is making different angle. Like that infinite angles as there are infinite internuclear vectors, each of them may be making different angles with respect to the magnetic field. Then what is going to happen is, if I consider the static situation I do not spin the sample at all, then I come across a situation this theta angle between internuclear vector 1 and 2 with magnetic field is not equal to theta 3, 4. If you put this sample different internuclear vectors are there with making different angles with respect to magnetic field. Then what is going to happen is, if I consider the static situation, I don't spin the sample at all, then what is going to happen is I come across a situation this theta 12, the angle between this internuclear vector and the magnetic field, is not equal to theta 34. Correct, if you put the sample, there are different internuclear vectors making different angles with the magnetic field. But on the other hand when I start rotating the sample what is going to happen is the time average, the ensemble average is such that the average orientation if you consider for this type of internuclear vector theta 12 or any internuclear vector theta 34 anything you consider, all internuclear vectors, it appears as if they all aligned along the direction of the spinning axis. This makes 54.7 degree with respect to the magnetic field. That means you have artificially created a situation by spinning the sample rapidly, that all internuclear vectors are aligned along the direction of axis of the spinning, which makes an angle 54.7 degree with respect to magnetic field. All internuclear vectors you can assume are all along this spinning axis which makes 54.7 degree.

So for chemical shift anisotropy magic angle spinning, the average long axis of an ellipsoid is now aligned along the spinning axis. If you consider CSA you have an ellipsoid the average long axis of the ellipsoid or internuclear vector in the case of dipolar coupling. All of them you can deem it to be aligned along magic angle.

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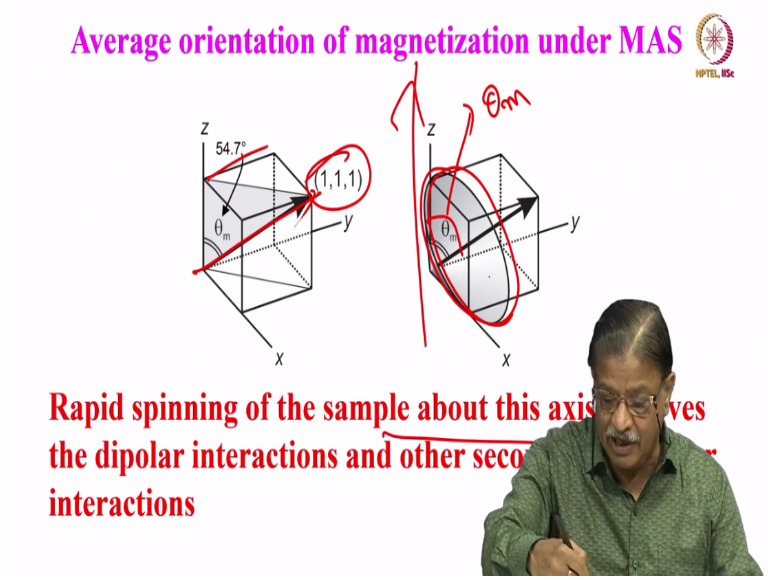

Average orientation of magnetization under MAS

Rapid spinning of the sample about this axis ves the dipolar interactions and other seco r interactions

So, if you consider the average orientation the magnetization under magic angle spinning, let us consider a cuboid. I have cuboid 1, 1, 1 which is the direction of the cuboid here; which makes angle with body diagonal of the cuboid. Imagine in the drawing, this is body diagonal of the cuboid, which makes with respect to magnetic field an theta m, which is nothing but the magic angle. It is a cuboid 111 and find out the body diagonal of it, and find out what is the angle it makes with respect to the magnetic field, which is along z axis.

Then you find out it is 54.7degree. That is what happens; the rapid spinning of the sample about this axis removes all dipole interactions and all second order interaction tensors when you are spinning at this angle.

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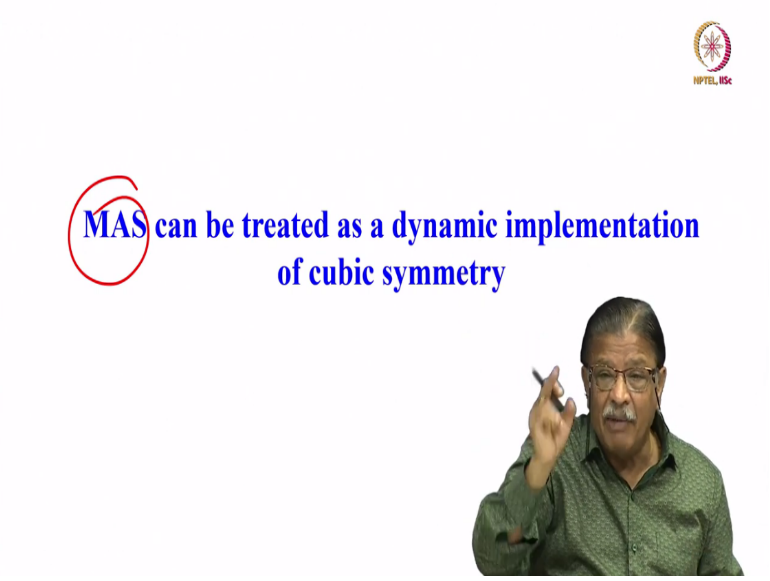

MAS can be treated as a dynamic implementation of cubic symmetry

So, what do you mean by this? if you had to understand this, it means the magic angle spinning can be treated as a dynamic implementation of the cubic symmetry. In the previous cuboid, the cubic symmetry is there and then if you start spinning the sample rapidly you can imagine all the internuclear vectors or the long axis of the ellipsoids in case of CSA; they are all aligned along the body diagonal of the cuboid, which makes in turn the magic angle 54.7 degree with respect to magnetic field or the spinning axis.

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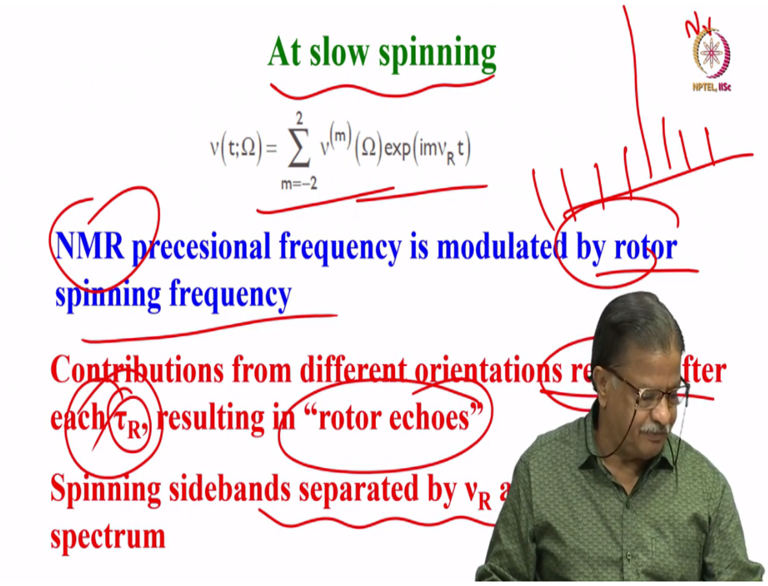

At slow spinning

$$\nu(t;\Omega)=\sum_{m=-2}^{2}\nu^{(m)}(\Omega)\exp(im\nu_R t)$$

NMR precesional frequency is modulated by rotor spinning frequency

Contributions from different orientations re fter each τ_R, resulting in “rotor echoes”

Spinning sidebands separated by ν_R a spectrum

Now what happens if I spin at different speeds. I need to have certain spinning speed I will come to that later. Supposing I have a very slow spinning I showed you several examples, I have a rotor spinning at 5 kilohertz, 10 kilohertz, 30 kilohertz, 60 or 100 kilohertz, like that. If I start spinning at a slow spinning speed, then what is going to happen is, the precessional NMR frequency gets modulated with the rotor spinning frequency, it interferes.

NMR precision frequency gets modulated by the rotor spinning frequency by this equation. I did not go into the details do not worry, it gets modulated. And contribution from different orientations refocus at each rotation, at tau r, which is called rotary echoes. Rotary echoes are the ones in which different orientations refocus, after each rotation. And as a consequence we get spinning sidebands separated by spinning frequency in the spectrum. What I mean is supposing this is the peak I am supposed to get. Now I start spinning at a slow speed, at a spinning speed nu R. Then at exactly integral multiples of spinning frequency, I am going to get what are called sidebands; these are called spinning sidebands; The spinning side bands will be at the frequency of the spinning speed, at which you are rotating the sample.

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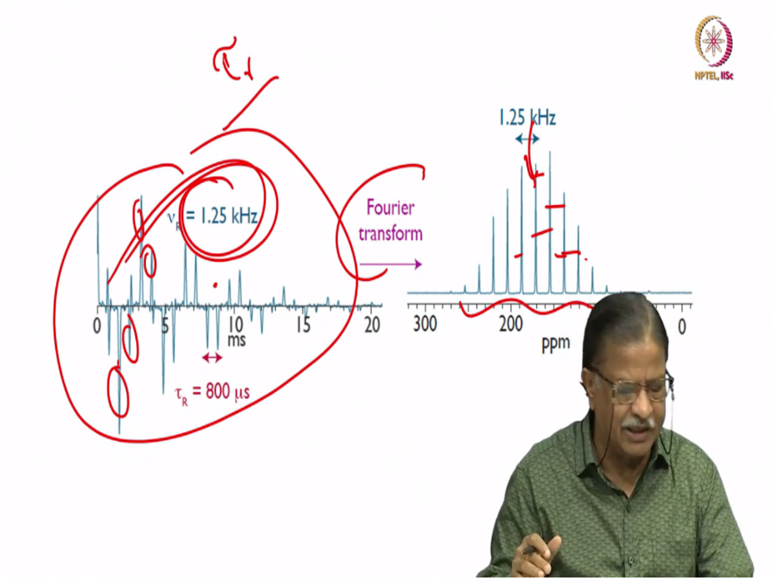

Look at this example, the free induction decay this is collected by spinning the sample only at 1.25 kilohertz. What are these things you are getting? It is not the frequency domain spectrum, it is a time domain signal. These are all called rotary echoes. At each 1 over tau r you are going to see this type of refocusing; and if you do the Fourier transformation of this time domain signa,l you get a frequency domain signal like this, the frequency domain spectrum.

Now you measure the separation of any of them; this correspond to spinning frequency. This is what it is. These are called spinning sidebands which comes at exactly at the integral multiples of the spinning speed. Now you may ask me where is my peak from my sample? we will come to that later. If this is our sample, with respect to that we can find out all the sidebands of separate on either side by the integral multiple of spinning speed; like omega nu R, 2 nu R, 3 nu R similarly – nu R – 2 nu R, like that.

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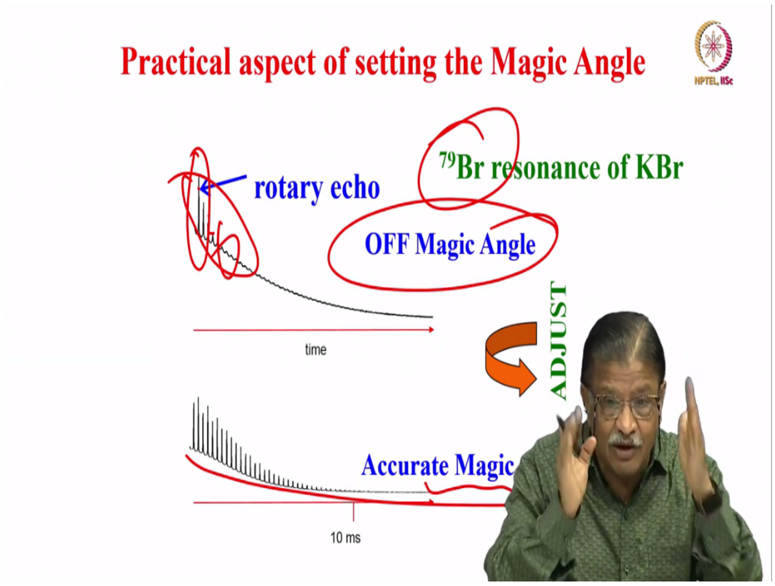

Practical aspect of setting the Magic Angle

^{79}Br resonance of KBr

rotary echo

OFF Magic Angle

ADJUST

Accurate Magic

So, magic angle how do you set it then? It has to be extremely precise. Remember, slight deviation from the magic angle we are bringing in the dipolar coupling or other anisotropic interactions. What normally is done is, we take the bromine resonance of potassium bromide and look at the rotary echoes. This is what I just now explained to you. These are called rotary echoes. Do not spin at a very high speed. Spin at certain normal speed, normal rotation frequency, spinning frequency like 4 kiloherz or 3 kilohertz or 5 kilohertz and start looking at the rotary echoes like this. Then you can start varying the angle, in a magic angle probe. There is the way, there is a provision for you to change the angle. Keep on changing. If the number of rotary echoes what you see are very much less that means you are off magic angle. You keep on tuning such that you get more number of rotary echoes like this, then more the number of rotary echoes you are getting the accurate the magic angle, you are coming very close to magic angle that is what it is.

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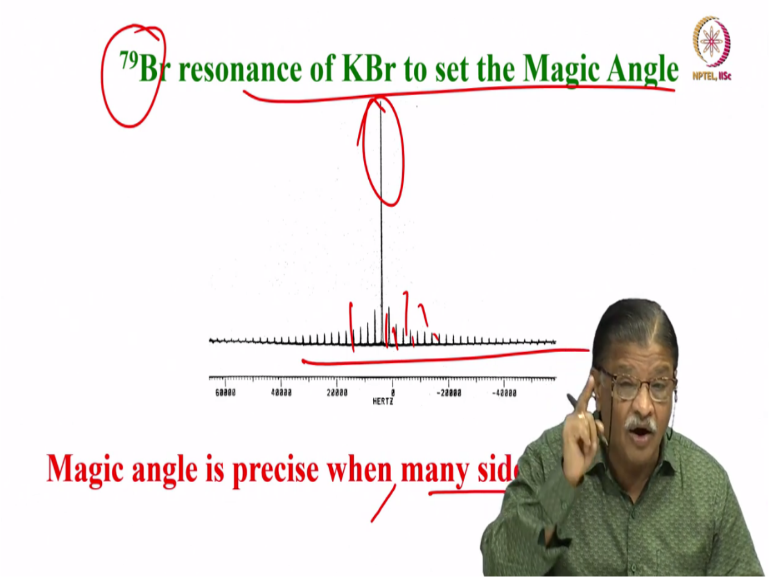
^{79}Br resonance of KBr to set the Magic Angle

Magic angle is precise when many sid

So bromine resonance of the potassium bromide, if it is taken and we set the magic angle this is how the spectrum comes. This is the central frequency corresponding to bromine 79 resonance of potassium bromide. And these are all sidebands. Larger the numbers of sidebands then you are more accurate with respect to spinning speed. If the sidebands are only few when you are spinning at moderate frequency of 3 or 4 kilohertz in the potassium bromide; then you can be rest assured you are very much off from the magic angle. So, this is important when you are close to magic angle in potassium bromine 79 resonance when you have lot of sidebands.

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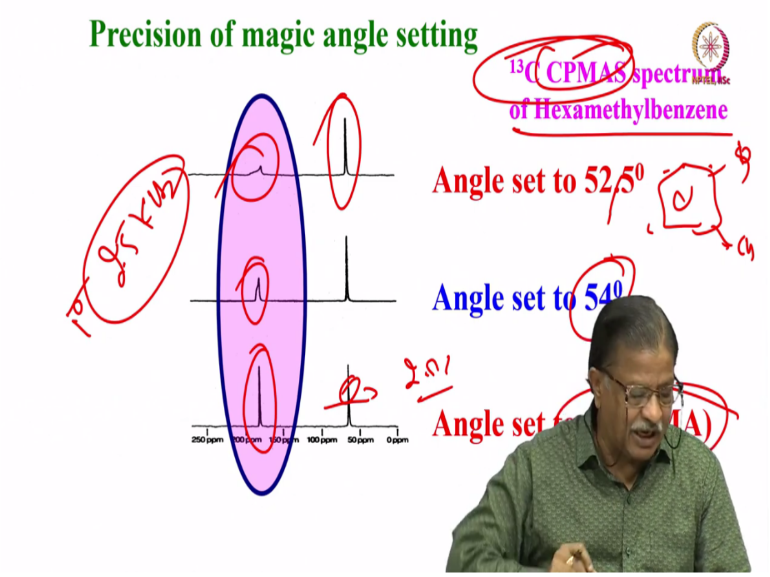
Precision of magic angle setting

^{13}C CPMAS spectrum of Hexamethylbenzene

Angle set to 52.5^{0}

Angle set to 54^{0}

Angle set t

How precise has to be magic angle, that can also be understood in a different way. Another sample which is normally used to understand the magic angle setting and also decoupling power, I will come to that later. It is the carbon 13 NMR spectrum of Hexamethylbenzene what is CPMAS? I will come to that do not worry this is by using Hexamethylbenzene. You look at the Hexamethylbenzene; Hexamethylbenzene has two types of carbons like this. And we have 6 CH3s and 6 quaternary carbons. So these are all the CH3 peaks, all CH3 are equivalent and this is a quaternary carbon. There are two peaks only you get, two carbon peaks. See now when you are exactly at the magic angle which is 54.7 degree you are going to get two peaks well resolved; look at the sharpness. Now slightly deviate by 0.7 degree not even 1 degree, just by 0.7 degree, 54 degree. This already distorted CO peak drastically. This is what it is. We concentrate at the CO peak to set the magic angle precisely. I just go one or two degrees away this peak completely disappears. It is very sensitive to magic angle and just I tell you move away from the magic angle just by one degree you are bringing in 2.5 kilohertz of the linewidth into this spectrum. The spectrum which is so sharp now if we just go one degree away from the magic angle, this line width will be 2.5 kilohertz more; that is what happens. So, the magic angle setting has to be very precise and it is little tricky so you have to understand this one.

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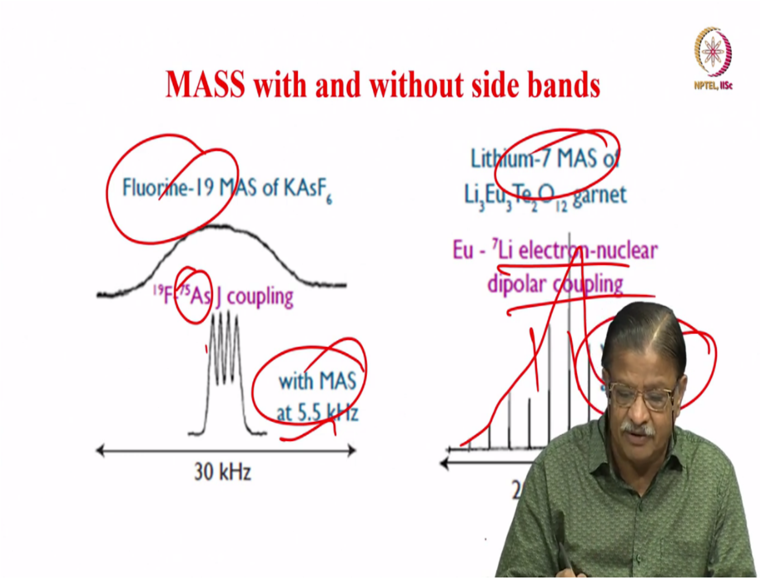

MASS with and without side bands

Fluorine-19 MAS of KAsF$_6$

^{19}F-^{75}As J coupling

with MAS at 5.5 kHz

30 kHz

Lithium-7 MAS of Li$_3$Eu$_3$Te$_2$O$_{12}$ garnet

Eu - ^{7}Li electron-nuclear dipolar coupling

This is a spectrum of a sample; just for understanding purpose I am showing you. This is fluorine 19 magic angle spinning spectrum of KAsF6. You are going to see the magic angle spinning spectrum at 5.5 kilohertz. You get four peaks which is where you are going to get fluorine 19, you are seeing the coupling with arsenic also. This is the lithium 7 MAS magic angle spinning spectrum. This is the molecule and we are spinning at 20 kilohertz; lots of sidebands you are going to see; sharp peaks. If you do not spin it, you get a powder pattern which is like a profile like this; on the top of these sidebands or each peak you can join and you generate a broad spectrum that is a powder pattern. If we do not spin the sample this is what you are going to get in a static case, but when you start spinning they break into sidebands like this. This is the spectrum of magic angle spinning without sidebands. This is with sidebands; here there are no sidebands.

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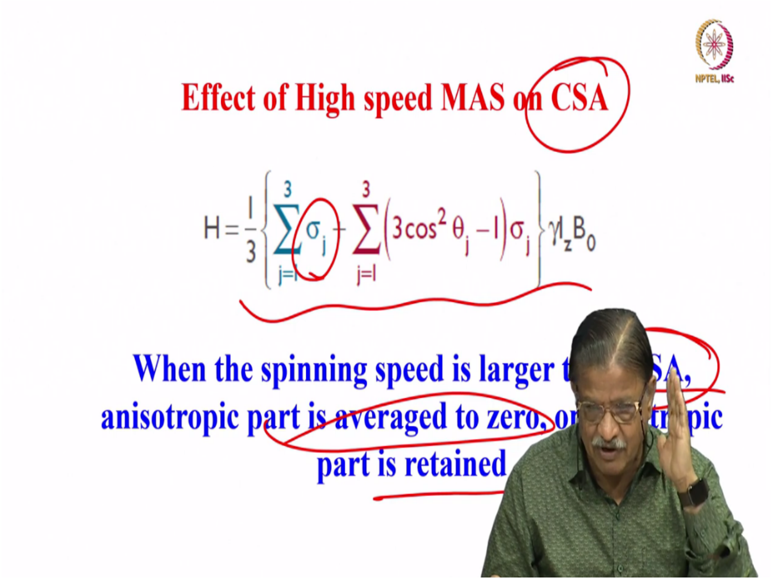

Effect of High speed MAS on CSA

$$H=\frac{1}{3}\left\{\sum_{j=1}^{3}\sigma_j+\sum_{j=1}^{3}\left(3\cos^2\theta_j-1\right)\sigma_j\right\}\gamma I_z B_0$$

When the spinning speed is larger t SA,
anisotropic part is averaged to zero, o tr pic
part is retained

Another very important thing; what is the effect of high speed magic angle spinning on chemical shift anisotropy? What should be the spinning speed? First, what happens if I spin at the high spinning speed. This is the Hamiltonian when the spinning speed is larger than the chemical shift anisotropy, I am concentrating on chemical shift part here. When the spinning speed is larger than chemical shift anisotropy, the anisotropic part is averaged to 0 and only isotropic part is retained. If it is not larger than that what happens like we saw in the previous example you get sidebands. The spinning speed, especially when you are concentrating on the chemical shift anisotropy, should be larger than chemical shift anisotropy. Only then anisotropic part is averaged out and isotropic part is retained.

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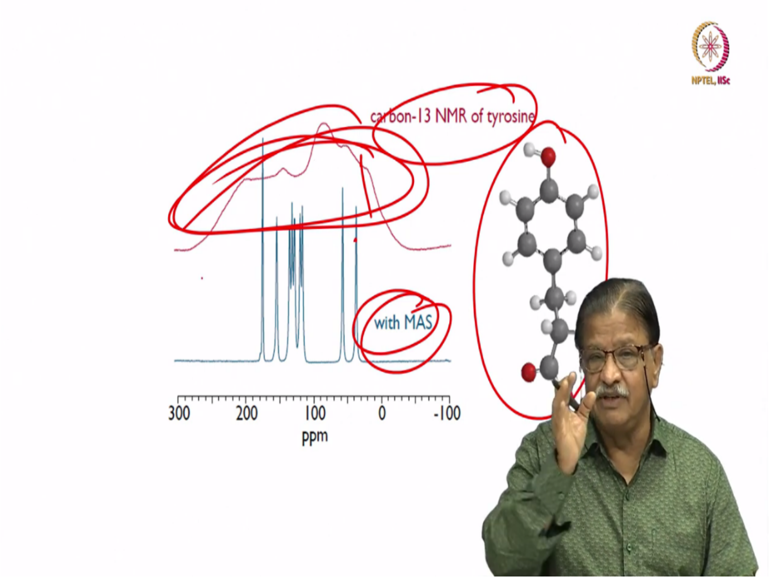

This is an example of a spectrum of tyrosine taken from the literate. You see this is a powder pattern without spinning. As soon as it starts spinning with magic angle spinning look at it how sharp length you are going to get. Of course, it is no way comfortable to liquid state NMR spectrum where the line width is of the order of 0.2 hertz or 0.1 hertz. But here line width is still quite large 40 to 50 hertz will be there. But nevertheless you can see, compared to powder pattern they are very sharp lines, when you start spinning at the magic angle. Here the spinning speed is larger than this width of the powder pattern, only then you will not get into sidebands, you get only sharp peaks. Each peak corresponds to individual chemical shift of the particular carbon.

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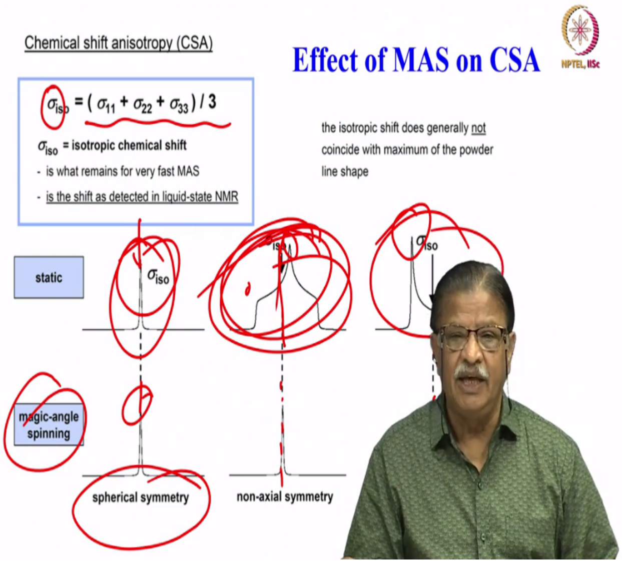

Chemical shift anisotropy (CSA)

Effect of MAS on CSA

$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33}) / 3$

σ_{iso} = isotropic chemical shift

- is what remains for very fast MAS
- is the shift as detected in liquid-state NMR

the isotropic shift does generally not coincide with maximum of the powder line shape

So, now with this knowledge we will understand what is the effect of magic angle spinning on chemical shift anisotropy. Chemical shift anisotropy in the isotropic part, as always I was telling you, it is average of all the three orientations of principal components of CSA. That is sigma 11 plus sigma 22 plus sigma 33 divided 3; that is average orientation that is isotropic chemical shift.

But as I said in the powder pattern whether it is axially symmetric or asymmetric all the three components are present. In the axially symmetry case two are equivalent, but axially asymmetric case all the are different. And this is static sample if it consider, the isotropic sample no problem or if you take a molecule which has spherical symmetry, we took the example earlier you see, when you take the example of a molecule with a spherical symmetry, then it will give a sharp peak even in the static case; that is what you remember we saw that when we were discussing axially symmetric tensor and everything for CSA. This is sharp peak, and this is the spinning at the magic angle, makes no difference in this case. You get the same little bit reduction in the linewidth could be there, but you are going to get same isotropic chemical shift, no change at all.

Look at this one powder pattern, which is axially asymmetric. You start spinning at a rate faster than the width of the powder pattern you are going to get a peak single peak, it is somewhere here; this corresponds to isotropic chemical shift of this. And then you get a single peak. Remember isotropic chemical shift need not be exactly one of the kinks here; sigma 11, sigma 22, sigma 33 they are different values. So, isotropic shift can be different so similarly sigma for the axially symmetric case; this is the powder pattern and when you start spinning this is how we get the spectrum.

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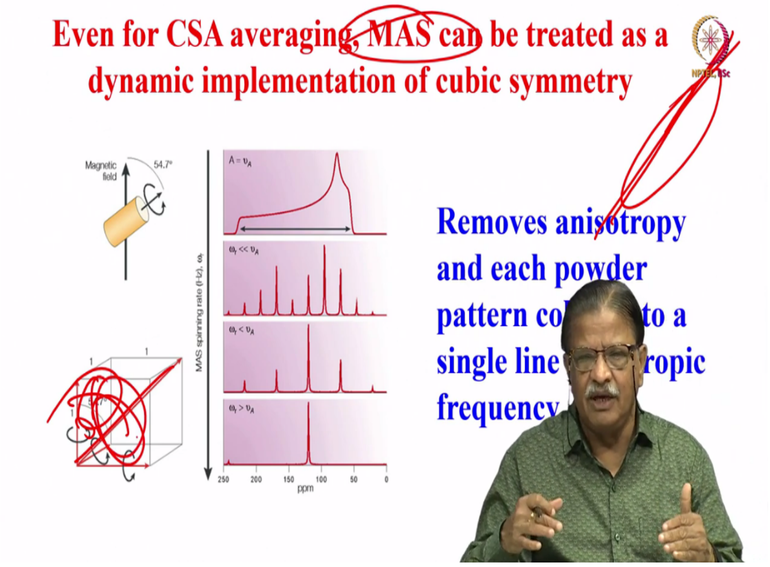

Even for CSA averaging, MAS can be treated as a dynamic implementation of cubic symmetry

Removes anisotropy and each powder pattern co to a single line ropic frequency

So even for chemical shift averaging similarly, it is analogous to magic angle spinning it can be treated as the dynamic implementation of the cubic symmetry. Again we saw the cubic symmetry we understood the body diagonal of it makes 54.7 degree with respect to this Z axis which is, let us say, along the magic angle. We saw the internuclear vector in the dipolar coupling case, it is a dynamic implementation of the cubic symmetry. I also mentioned if you consider the ellipsoid for the CSA, the long axis of the ellipsoid can be thought as if it is align like this and the CSA averaging out can also be treated as dynamic implementation of the cubic symmetry; that is what it is.

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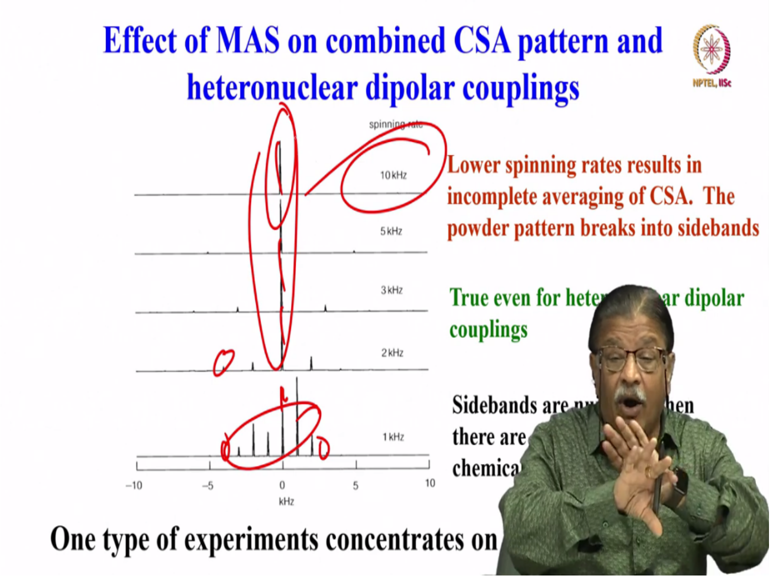

Effect of MAS on combined CSA pattern and heteronuclear dipolar couplings

Lower spinning rates results in incomplete averaging of CSA. The powder pattern breaks into sidebands

True even for hete ar dipolar couplings

Sidebands are hen there are chemica

One type of experiments concentrates on

So, now if you want to see the effect of magic angle spinning on the combined chemical shift anisotropy pattern and all heteronuclear dipolar couplings, because in a system they are not too independent parameter; everything would be there. In a molecule we have a CSA we have a heteronuclear dipolar coupling, homonuclear dipolar coupling varieties of things would be there. So, we will see now in the example like this what happens in a situation when you have chemical shift anisotropy and heteronuclear dipolar couplings both are present. This is where that sample is spun at 1 kilohertz you see lot of sidebands here. So, this will be the separation of the sideband frequency which correspond to spinning frequency which is one kilohertz. Here the separation is 2 kilohertz which correspond to spinning frequency. This separation is 3 kilohertz, this is the spinning frequency like that. We come to 10 kilohertz we do not have any spinning sideband at all. So, what does it mean as we increase the spinning speed; when the spinning speed goes beyond the CSA or heteronuclear dipolar coupling, then you will not get any sidebands. They all merge into centre band; that is the isotropic chemical shift. You can see only one peak which is not moving, at all the spinning speed.

You can start spinning the sample at different speeds like this. But every time you can see one interesting thing, you must understand, whatever you do the isotropic peak will not change whatever be the spinning speed. See this is remaining same, whereas the sidebands are moving away this must be remembered. If you want to identify what is your chemical shift what is isotropic chemical shift frequency, what you have to do is if there are too many sidebands spin at two different spinning speeds.

The peak which does not move with different spinning speeds is your isotropic chemical shift. All other peaks which keep moving away with different spinning speeds; they are a sidebands. So, this is what you should understand. When you take the example of both heteronuclear dipolar couplings and chemical shift anisotropy are present; when you start spinning at a rate faster than this heteronuclear interactions strength, dipolar coupling strength or CSA, you are going to get a single peak devoid of all sidebands; that is important thing.

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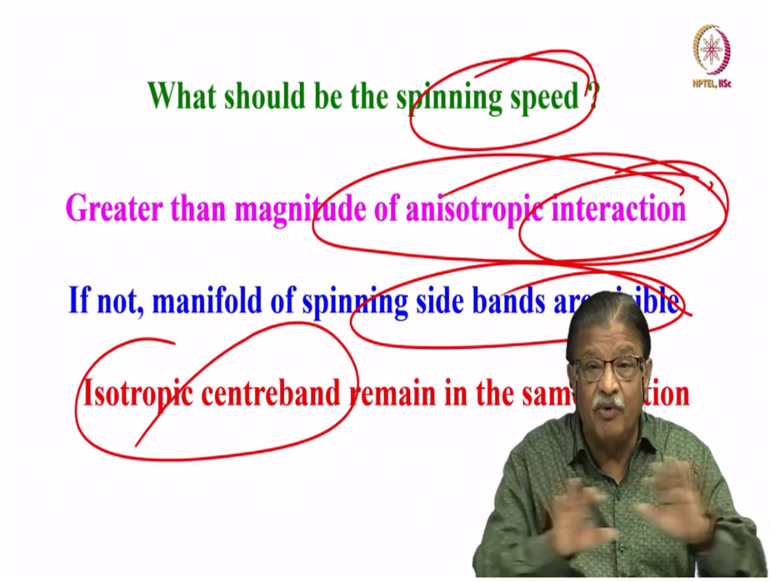

What should be the spinning speed ?

Greater than magnitude of anisotropic interaction

If not, manifold of spinning side bands ar ible

Isotropic centreband remain in the sam tion

Remember spinning speed that is what I am asking the question now, what should be the spinning speed? that is what we discussed now. It should be greater than the magnitude of the anisotropic interactions. It could be CSA or heteronuclear dipolar coupling. You may ask me what is homonuclear dipolar coupling? that cannot be eliminated by magic angle spinning alone, I will come to that later, that is not possible to eliminate, which is homogenous interaction we will come to that part later.

But right now when you are concentrating only on the magic angle spinning the anisotropic interactions; that is chemical shift anisotropy and heteronuclear dipolar couplings are the two parameters which can be eliminated, when you start spinning the sample whose spinning speed is greater than the magnitude of these anisotropic interactions. That is it should be larger than heteronuclear dipolar coupling or larger than CSA.

How do you know what is CSA? or what is heteronuclear dipolar couplings? you do not know off- hand. Keep on increasing the spinning speed till the sidebands disappear; that is what you have to do. So, if you spin at a rate lower than that the sidebands they are visible and as I said isotropic centre band will remain same irrespective of the spinning speed; whereas the sidebands start moving away.

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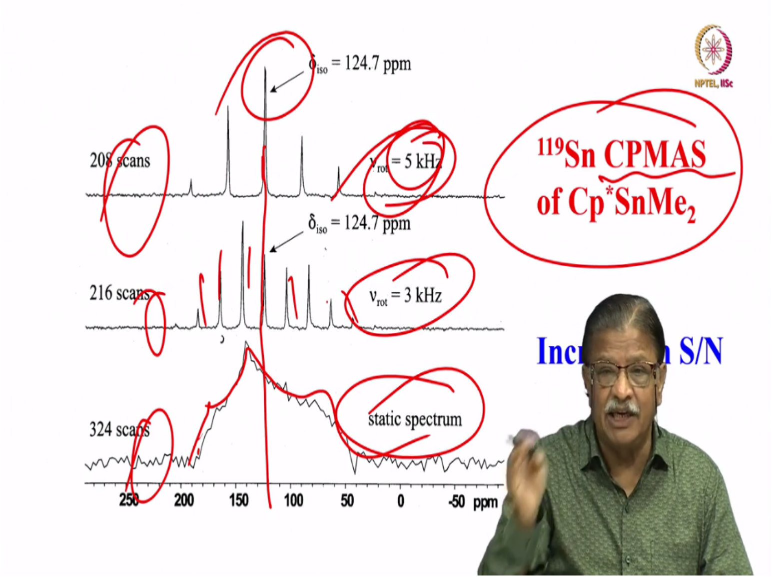

^{119}Sn CPMAS of Cp*SnMe$_2$

Inc   S/N

So, this is what I wanted to tell you. Just to show you an example of a spectrum like this, this is some spectrum of Tin 119 CPMAS spectrum. What is CPMAS? do not worry, I will come to that, again I am telling you. Tin 119 spectrum of this molecule; this is a static sample that means no spinning. You see there is a profile of a powder pattern; it looks like a powder of a axially asymetric tensor, you can see that. This is CSA pattern.

Now start spinning at 3 kilohertz. Spinning speed is 3 kilohertz magic angle spinning speed; now you have sidebands like this, lot of sidebands are there. Now increase thee spinning speed to 5 kilohertz from 3 to 5 khz, what should happen the centre band should not change at all; that is remaining same. Remember centre band can be anywhere here in powder pattern it need not be at the kink as I told you.

So, centre band is here; that is not changing with the spinning speed. This is a isotropic chemical shift. So, if you want to identify isotropic peak, do the experiment at two spinning speeds; orgo to very large spinning speed, remove the sidebands. And now what is another interesting thing you must observe when you remove this spinning sidebands by spinning at higher frequencies, you see signal to noise ratio increases here.

Look at the signal to noise ratio; compared to the signal to this noise ratio, compared to this at 5 kilohertz, you see there is enormous increase in signal to noise ratio. There is increase in signal to noise ratio, it has become better by going to higher and higher spinning speeds.

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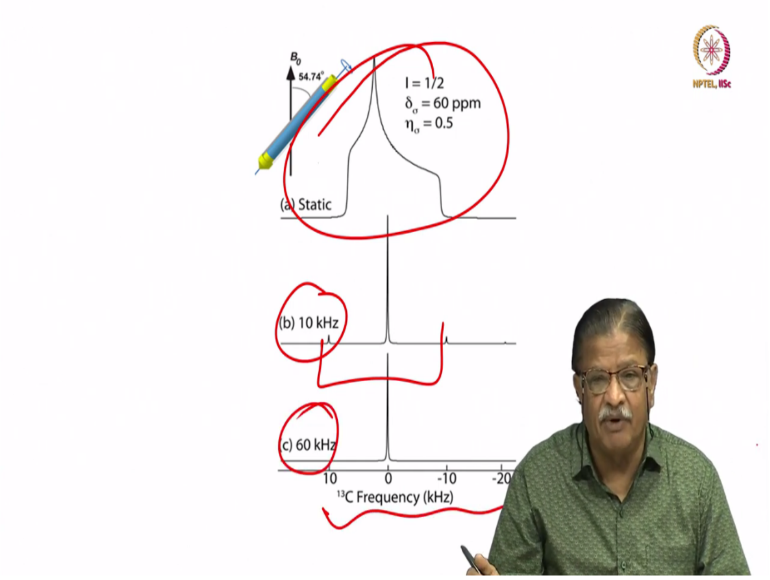

And this is the spectrum of one of the molecules. Look at it; this is the static sample for spin half nucleus. And you start spinning at 10 kilohertz; this is what the spinning speed and sidebands; this is the powder pattern static case. If we spin at 60 kilohertz, you see in the carbon 13 NMR absolutely no sidebands, completely removed. You have only one peak at the isotropic chemical shift position.

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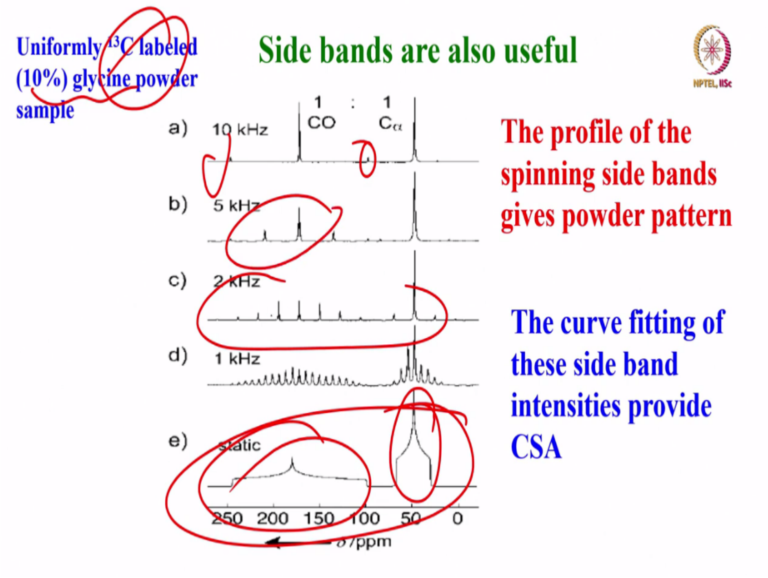

Uniformly ^{13}C labeled (10%) glycine powder sample

Side bands are also useful

The profile of the spinning side bands gives powder pattern

The curve fitting of these side band intensities provide CSA

So, this is what I wanted to tell you we are removing the sidebands. But we can also use sidebands. If you spin at a lower spinning speed like this; 1 kilohertz, 2 kilohertz you get sidebands. We can do curve fitting of the sidebands then you ask me what do I get? This is a static example of a sample glycine powder. See this is for C alpha and this is CO carbon see both are axially assymetric tensor, static case. Start spinning at sidebands. And now if you go to very high spinning speed you will remove these things; also and you get only isotropic chemical shift. If I spin at a speed like this; 2 kilohertz or 5 kilohertz, I get sidebands. I can do the curve fittings. If I do the curve fittings, I also get what is called chemical shift anisotropy. It is useful for me, I can get information of the charge density distribution at the site of the given nucleus. So, CSA can be obtained. So sidebands are also useful. So, since the time is getting up I am going to stop here. What I wanted to tell you today is, we started discussing about magic angle spinning. I said there are varieties of magic angle spinning rotors available which are made up of material called Zirconium oxide, silicon nitride; varieties of things are there. Zirconium oxide rotors are commonly utilized and then put the sample in a rotor of various dimensions, 2.5 mm, 1.3, 2.5 mm, like that varieties of internal diameters rotors. As the size of the rotor, the internal diameter, becomes smaller and smaller spinning speed becomes larger and larger, but at the same time quantity that you are going to use becomes smaller and smaller, as the size of the rotors becomes smaller. These are all things which you have to arrive at the comprise. And then when you start spinning a sample by putting a rotor at an angle with respect to the magnetic field in a probe; and when we start spinning at larger speed, it is as I said analogous to dynamic implementation of the cubic symmetry. In other words, consider a cuboid different internuclear vectors are making different angles with respect to the magnetic field. Now once you start spinning at a rapid speed all different infinite number of different internuclear vectors making different angles with respect to magnetic field, you can deem it to be aligned along the spinning axis, which is along the body diagonal of the cuboid, which makes 54.7 degree with respect to the magnetic field. This is called magic angle. And I said magic angle eliminates heteronuclear dipolar couplings; chemical shift anisotropy. These are the very important things and spinning speed should be larger than the interaction strengths. It should be larger than the heteronuclear dipolar couplings, it should be larger than chemical shift anisotropy. If it is smaller than that you get number of sidebands. Powder pattern breaks into sidebands. Powder pattern is what you are going to get in a static case, without spinning.

If you start spinning at a lower speed you get number of sidebands. Start spinning at a larger speed much larger than interaction strength you will get only isotropic chemical shifts. If you do not have such a facility to spin at larger speed; then you do at two or three spinning speeds. Then the center band will remain at the identical frequency; it will not vary with the spinning frequency. Whereas the sideband keeps moving away. This is how we can utilize this method to identify the center band. So, I took some of the examples to show how spinning speed will change from the powder pattern we are going to get sharp peaks; and how the signal to noise ratio increases and everything. And I also said sometimes the sidebands at lower spinning speed are useful, use it, do the curve fitting you can see CSA values; which are useful. It will through information on the charge density distribution at the site of the given nucleus. These are the things what we discussed. We will come back. In the next class I will discuss further from this point. Thank you very much; I will stop here.